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Transforming biogas into biomethane using membrane technology

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ABSTRACT

Upgrading biogas, i.e., the removal of CO_2 from CH_4 is an attractive regenerative energy as it is supplied continuously. Conventional upgrading techniques such as absorption or adsorption require significant amounts of energy and require equipment of large size. Hence, we give an overview on gas permeation membrane processes which are applied in biogas upgrading. Here, we consider the upgrading process as a whole. The multiscale design of membrane-based gas separation is analyzed in detail. Membrane materials, gas permeation modules and their respective operation as well as gas permeation processes for biogas upgrading are investigated. Applying gas permeation modules, compression of the feed gas should be used since it is energy efficient for gases with high amounts of CO_2. Single stage gas permeation processes are not able to produce a high CH_4 purity and simultaneously obtain a high CH_4 recovery. Hence, multistage concepts are mandatory. Membrane-based upgrading systems are an interesting alternative to conventional biogas upgrading equipment and we expect that they will significantly contribute to the energy supply of the future.

Contents

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1. Introduction

The transition from a fossil-based energy supply to energy generation from renewable resources is mandatory but still pending [1]. Using biogas generated from organic substances can support this transition [2]. In Europe, the biogas production in 2007 was 69 TWh (for comparison: 600 MW coal fired power plant 5 TWh) [3] but the economic potential is not exploited, yet [4].

Biogas is either used in combined heat and power engines (CHP) or it is used as a natural gas substitute by removing CO_2 from CH_4. Today, most biogas plants operate by combusting the gas on-farm in CHPs, which is inefficient when the produced heat cannot be utilized. Hence, the electrical power efficiency is less than 40% [5–7].

Upgrading the raw biogas, which is often referred to as biomethane, and supplying this gas to the natural gas grid, seems an attractive alternative to its utilization in CHPs. Biomethane can be used for both energy generation and as feedstock for the chemical industry [8]. In contrast to on-farm CHPs, the supply of biomethane to the natural gas grid and the subsequent utilization of the gas in combined large size heat and power cycles is more efficient as the generated heat is utilized by customers demanding large quantities of heat, such as district heating or industrial customers [9].

Recently, first biogas upgrading plants were installed in Europe and in the US [10,11] using technologies from the chemical process industry and natural gas treatment to remove CO_2 from CH_4. These technologies are well established but have drawbacks such as the large size of the equipment required and its high energy demand. Membrane technology is an alternative to conventional gas separation processes as gas permeation membranes address most of the aforementioned drawbacks.

Thus the present study is a review of membrane-based biogas upgrading systems. As shown in Fig. 1, membrane processes have to be designed with a multiscale approach. Appropriate membrane materials, as well as an efficient module and process design, determine the competitiveness with conventional separation technology. In this study, various membrane materials will be presented. Commercial gas permeation module suppliers and their corresponding module designs will be identified. The main focus of the present study is the membrane-based process design which includes single and multistage gas permeation processes as well as hybrid processes in which gas permeation modules are combined with conventional separation equipment. Ultimately, a reflection on the future perspectives of membrane-based biogas upgrading will be presented.

2. The potential of biogas in the energy supply of the future

Biogas is generated by the digestion of organic matter in

- sewage plants,
- landfills,
- industrial wastes,
- agricultural production.



Fig. 1. Characteristics of membrane process design. First a membrane material has to be selected. Then an adequate module has to be chosen, and finally the module has to be integrated into the process.

Hence, biogas can be used as an energy source in industrialized as well as in developing countries.

The world energy demand in 2050 will be more than 1000 EJ/a. Resch et al. [12,13] report that the bioenergy use in 2004 has been 50 EJ. However, they distinguished between four different energy potentials, which are the theoretical, the technical, the realizable, and the mid-term potential. For energy supplied by biomass, they report a theoretical potential of 2900 EJ and a technical potential of 250 EJ. McKendry [14] notes that biomass has currently a share of 10–14% in the world's energy supply.

Other studies note that bioenergy will contribute 10% to the future energy supply [15]. The share of biogas is expected to be 25% of the total bioenergy [16].

Although the contribution of biogas to the future energy mix seems to be marginal, it is an important energy source in some regions [17–19]. In contrast to solar and wind based energy supplies, biogas is produced continuously, so that it can be used for a base load energy supply.

3. Process description

The size of biogas plants in rural areas is limited by the economics of transporting the material for digestion [20,21]. Typical biogas plants generate raw gas flow rates of less than 4000 m^3/h [5]. The raw gas leaves the fermenter at a pressure of about 1.1 bar and a temperature of 30 °C.

Fig. 2 shows the process steps in biogas upgrading. The biogas is generated in a fermenter and the biogas leaves the fermenter saturated with water. The most important cleaning step is CO_2 removal, which is referred to as upgrading the biogas. In addition, water vapor and H_2S have to be removed. Subsequently, the upgraded and cleaned biogas is compressed and injected into the natural gas grid as a natural gas substitute. The sequential arrangement of the various process steps shown in Fig. 2 depends on the corresponding upgrading technology [5].

Table 1 illustrates the biogas composition when the raw gas leaves the fermenter. The raw biogas consists mainly of CH_4 and CO_2 and the composition is highly dependent on the biogas source and the applied substrate for fermentation [22,23]. Minor components such as H_2S or NH_3 are generated during fermentation and these components also have to be removed before the upgraded gas is fed to the natural gas grid.

In order to inject the gas into the natural gas grid, the gas has to be purified and it has to meet the corresponding pipeline specifications. Table 2 presents the pipeline specifications for natural gas injection in the US, in Austria, and in Germany. In the UK, no standard has yet been developed [24]. In the US the CO_2 content is specified, which has to be lower than 2 vol%, while in Germany the Wobbe-index is used to control the gas quality.

4. State of the art processes

Conventional CO_2 separation equipment is well established in the chemical industry. Processes such as physical and chemical

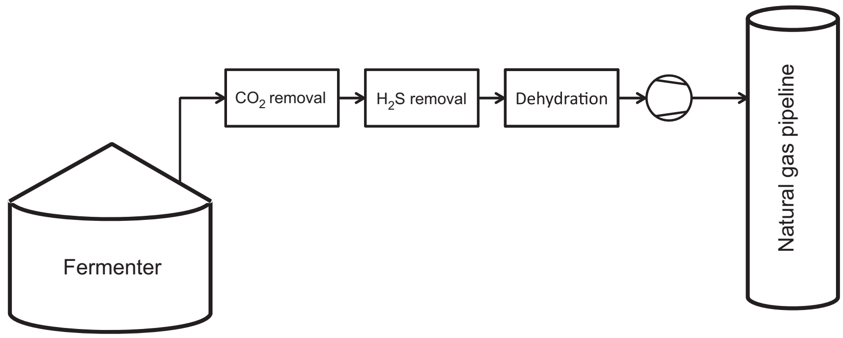


Fig. 2. Biogas upgrading process illustrating the required separating and polishing steps from the fermenter to the natural gas grid. CO_2, H_2S, and water vapor have to be removed before the gas is injected into the pipeline.

Table 1
Mole fractions of biogas components [10] prior to the upgrading. The typical range of biogas composition is given. A specified composition is presented prior and subsequent to compression. As water will condense during the interstage cooling, the mole fractions change significantly.

Component	Typical range
CH_4	0.45–0.75
CO_2	0.25–0.55
H_2O	0.031
N_2	0.0001–0.05
O_2	0.0001–0.02
H_2S	0.000006–0.02
Organic sulfur molecules	< 0.00002
NH_3	< 0.000006
Benzene, toluene, xylene	< 0.000001
Siloxanes	< 0.0000007

absorption as well as adsorption are used in biogas upgrading [29].

Fig. 3 depicts an absorption process in which amines are used to remove the CO_2. An absorption column and a desorption column are combined so that the amine solution can be regenerated continuously. The amine solution is regenerated by heating the liquid using steam. The CO_2 is stripped from the amine solution.

The advantage of amine scrubbing is that high CH_4 purities ($>95\%$) and low CH_4 losses ($<0.1\%$) are achieved [10,5]. However, the application of amine scrubbing is energy intensive, as steam has to be supplied to regenerate the amine solution. Furthermore, the amine solution is sensitive to impurities of H_2S and thus H_2S has to be removed before the raw gas enters the absorption column. The amine scrubber operates at ambient pressure and the product gas is obtained at this low pressure, so that a subsequent compression is required. Amines are toxic and malfunction of the upgrading plant may harm the environment and have an impact on the humans and animals at the site. In addition, absorption columns are voluminous. The equipment size is not a crucial issue in biogas upgrading in agricultural production. However, the equipment size determines the capital costs.

A water scrubbing process is presented in Fig. 3. Two columns, one absorption column and one desorption column, are required. CO_2 is absorbed in the water at elevated pressures. The water is regenerated by decompressing the water and by feeding a stripping gas to the desorption column. Accordingly, no heat is required to remove the CO_2 from the water.

The pressurized water scrubbing process operates using only water as a solvent, which is more secure than applying chemical solvents. The absorption process is performed at elevated pressures so that the product gas is already pressurized. However, as water scrubbers operate basically at pressures of less than 10 bar, the upgraded gas has to be compressed to grid pressure. Since H_2S cannot be completely removed from the water in the regeneration some of the water has to be removed in order to prevent accumulation of sulfur components in the solvent. The selectivity of absorbing CO_2 and CH_4 is limited, which results in significant CH_4 losses.

In addition to the liquid separation processes, adsorption can be applied to capture CO_2 on solid surfaces [30–32]. Fig. 3 shows a typical pressure swing adsorption process. In general adsorption is a discontinuous process, but the application of multiple adsorption vessels transforms the discontinuous process into a continuous process. While one vessel is adsorbing the CO_2 molecules from the bulk CH_4 stream, the other adsorption vessels are regenerated. To adsorb CO_2 molecules, the raw gas has to be compressed. The loaded vessels are regenerated by lowering the pressure in the vessel and the adsorbed molecules desorb. Two types of adsorption mechanism can be used to separate CO_2 and CH_4, which depend on the solid material. Both rate limited and equilibrium limited adsorption are applied in industrial scale separation systems.

Using pressure swing adsorption, gases with high methane purities ($>$ 98%) are produced [5]. However, significant methane losses cannot be avoided as some methane also adsorbs on the solid surface. Some pressure swing adsorption suppliers have optimized the system using six vessels, and obtain methane recoveries higher than 98% [5]. The system is rather complex and it requires intensive control and maintenance due to its moving parts (control valves). As the pressure swing adsorption operates at moderate pressure, the purified gas has to be compressed in an additional compressor. Furthermore, there is a tradeoff between methane purity and methane recovery [10].

In order to obtain high purities for both gas components CO_2 and CH_4, cryogenic separation can be used [33,34]. However, this separation technique requires large quantities of energy as the gas mixture is chilled down to less than $-80\ ^{\circ}C$. The boiling point of CH_4 is at $-162\ ^{\circ}C$ and the sublimation of CO_2 is at $-78.5\ ^{\circ}C$ (both at standard pressure). The required CH_4 purity for natural gas grid injection is 96%, but the CH_4 purity obtained from cryogenic separation is significantly higher, which is inefficient. Moreover, cryogenic separation requires large processing equipment, and driving this process is demanding of energy. Accordingly, cryogenic separation is not used in biogas upgrading.

Detailed information on conventional upgrading equipment is available in [5,35]. Table 3 compares the various conventional upgrading processes in terms of electrical and thermal energy demand as well as in terms of specific upgrading costs. The energy demand corresponds to the flow rate of the product gas. The specific upgrading cost is related to the energy content of the product gas.

The aforementioned analysis of conventional process equipment for biogas upgrading indicates the following main drawbacks:

- The processes are energy intensive.
- The CH_4 rich product gas is at low pressure.

Table 2
Pipeline specifications when supplying upgraded biogas to the natural gas grid: German, Austrian, and US standards.

Component	Unit	Germany	Austria	US
Wobbe index	kW h/m^3	15 (12.8–15.7)	13.25–15.72	
Upper heating value	kW h/m^3	8.4–13.1	10.7–12.8	
Lower heating value	kW h/m^3	8.4–13.1	10.7–12.8	9.8–11.4
O_2 dehydrated gas networks	mol%	<3	<4	$<0.2-1$
O_2 not dehydrated gas networks	mol%	<0.5	<0.5	$<0.2-1$
H_2S	mol%	<0.0003	<0.0004	<0.00037
H_2O		< dewpoint	< dewpoint	< 120 ppm
CO_2	mol%			$<2-4$
Ref.		[25,26]		[27,28]

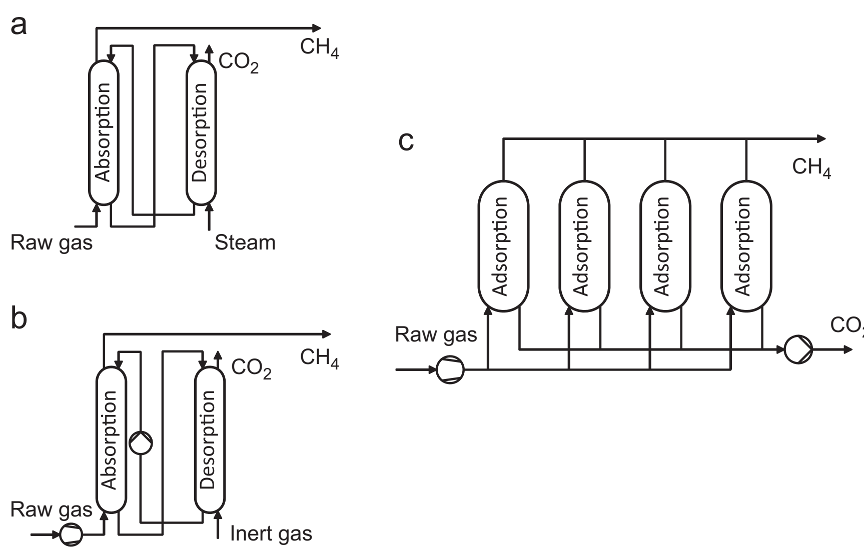


Fig. 3. State of the art biogas upgrading technologies. (a) shows an amine absorption process, (b) is a water scrubbing process and (c) is pressure swing adsorption.

Table 3
Comparing conventional upgrading equipment for CO_2 removal. Pressure swing adsorption (PSA), chemical absorption using amine scrubbing, and physical absorption applying pressurized water scrubbing are compared. The data is adapted from a technical report by Fraunhofer Umsicht [5].

	Unit	PSA	Amine scrubbing	Water scrubbing
Specific electrical energy demand[a]	kW h/m^3 (STP)	0.25	0.15	0.25
Specific upgrading costs[b]	Euro cent/kW h	1.31	1.35	1.25
Specific thermal energy demand	kW h/m^3 (STP)	0.7–0.75	0.3–0.8	—
Product pressure	bar	4–7	1.1	4–7
CH_4 recovery	–	0.97	0.999	0.98–0.99
Supplier	–	CarboTech Engineering (D), Cirmac (NL), QuestAir (CAN), Verdesis (CH)	DGE (D), MT-Biomethan (D), CarboTech (D), Cirmac (NL)	Flotech (S, NZ), Malmberg (S), YIT(S), RosRoca (D)

[a] Including compression up to 7 bar.
[b] Referred to the product gas.

- Complex systems involving several process steps are required to remove CO_2, H_2S, as well as H_2O, hence reducing the robustness of the system.
- Large equipment sizes.
- Associated materials such as water, amines, or activated carbon are required.

Membrane-based gas separation seems able to address these drawbacks. Typical advantages of gas permeation processes are [36,37]:

- High energy efficiency.
- Low capital costs.
- Robustness of the process.
- Ease of operation and maintenance.
- Small footprint due to high packing densities of membrane material in the respective membrane modules.
- Product gas already at natural gas grid pressure.

A membrane-based separation plant is mainly designed to remove CO_2 from the CH_4 bulk. However, trace components in the raw biogas such as hydrogen sulfide or water vapor permeate even faster through the membrane than CO_2 [38]. Therefore, gas permeation membranes could remove CO_2, hydrogen sulfide, and water vapor in one step if sufficient driving force for permeation is provided. Fig. 4 shows that in conventional biogas upgrading

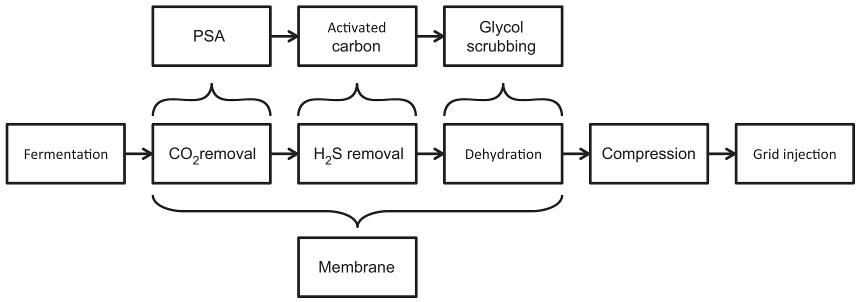


Fig. 4. The various unit operations in biogas upgrading are shown from the fermenter to the natural gas grid. Generally, each individual separation is done by one individual unit. The membrane system can perform the three separation steps in one step, which is an advantage compared to conventional equipment for CO_2 removal.

processes, the removal of single gas components is performed by individual units.

5. Membranes for biogas removal

Membrane-based biogas upgrading is an alternative to conventional upgrading technologies. In the recent past, gas permeation membranes have frequently been applied to natural gas treatment [28,37–43]. Therefore, it is reasonable to adapt these membrane processes to biogas upgrading [44,45], since the gas mixtures involved are similar. However, the process conditions in natural gas treatment and biogas upgrading are different. The natural gas is under pressure when it leaves the natural gas field whereas in biogas upgrading, the raw gas has to be compressed to the pipeline pressure.

Basically, two entirely different membrane processes can be applied for the separation of CO_2 and CH_4 which are the application of gas permeation membrane [35,46–49] and the application of membrane contactors [50–52], respectively. Since conventional membrane-based gas separation is commonly done by gas permeation, the present study focuses on gas permeation membranes as this technology is already a mature and is frequently applied.

5.1. Membrane materials

The membranes in biogas plants have to withstand harsh process conditions as significant quantities of H_2S and H_2O are present and the gas is pressurized. Thus, the membrane material has to be chemically resistant to those gases. Furthermore, the membrane material has to withstand pressures of more than 25 bar and temperatures of more than 50 °C.

Various membrane materials are able to separate CO_2 and CH_4 and both polymeric as well as inorganic materials can be used. However, in industrial scale gas separation, only polymeric membrane materials are applied [39], due to their low manufacturing cost compared to inorganic materials.

Basu et al. [53] have compiled and reviewed current membrane materials for CO_2/CH_4 separation. Table 4 presents these materials and their permeability P and CO_2/CH_4 selectivity, which is given in terms of the ideal separation factor:

$$\alpha = \frac{P_{CO_2}}{P_{CH_4}}. \quad (1)$$

The membrane materials are evaluated in terms of technology maturity. Here, materials which are commercially available and which are manufactured in large quantities are referred to as commercial. Materials which have recently been developed and are still under investigation are labeled as research.

Many of the recently developed materials show outstanding permeability and selectivity data, such as SAPO-34 membranes [54–56]. However, it is difficult to manufacture these materials in industrial scale quantities [56] and it is not expected that these materials can be manufactured in industrial scale quantities within the next few years.

Table 4
Membrane materials suitable for biogas upgrading were analyzed by Basu et al. [53]. The permeability is presented in Barrer. Polymers as well as mixed matrix membranes (MMM) can be applied. In contrast to polymeric membranes which are commercially available, mixed matrix membranes have not reached this stage yet and are under investigation.

Group	Material	CO_2 (barrer)	α (CO_2/CH_4)	Development
Polymer	CA	6.3	30.0	Commercial
Polymer	EC	26.5	1.4	Commercial
Polymer	PC	4.2	32.5	Commercial
Polymer	PDMS	2700.0	3.4	Commercial
Polymer	PI	10.7	42.8	Commercial
Polymer	PMP	84.6	5.8	Commercial
Polymer	PPO	75.8	6.9	Commercial
Polymer	PSf	5.6	22.4	Commercial
MMM	CNT-PDMS	190.0	5.6	Research
MMM	Silica nanoparticles-PSf (10% np)	9.2	24.5	Research
MMM	SWNT-PSf(10% SWNT)	5.2	18.4	Research
MMM	Cu-BPY-HFS-PI(30 wt)	10.4	27.5	Research

Polymeric membrane materials are commonly applied in gas permeation. The most frequently applied and suitable membranes for natural gas treatment are polyimides and cellulose acetate membranes [57,28]. However, cellulose acetate membranes are sensitive to water vapor. Without pretreatment, cellulose acetate membranes are unsuitable for biogas upgrading [28].

5.2. Conceptual process design

Fig. 8 presents the basic flowsheet of the membrane-based biogas upgrading process and the required unit operations when gas permeation membranes are applied. The raw gas is compressed to the required pipeline pressure. The pressure is slightly higher than the pipeline pressure in order to overcome the pressure losses in the upgrading equipment and the piping system. Subsequent to the compression, the gas flows to a heat exchanger to control the gas temperature and to avoid high temperatures in the membrane system. Then the gas enters the membrane system to purify the gas. A fine desulfurization unit lowers the hydrogen sulfide level when the membrane system is not able to achieve the required hydrogen sulfide level. Finally, the purified methane reaches the natural gas grid.

6. Membrane modules

For gas permeation, three types of modules exist: hollow fiber modules, spiral wound modules, and envelope type modules [58].

Table 5 presents and evaluates the various types of gas permeation modules.

Due to the high packing densities, the application of hollow fiber and spiral wound modules is common. The gas is compressed before it enters the membrane system. The compression equipment has to be protected from particles as well as liquids and the corresponding components are removed prior to compression. Hence, hollow fiber modules can be used without further pretreatment. Table 6 depicts the membrane module suppliers for treating natural gas streams with the module type and the polymer used to separate CO_2 and CH_4, respectively.

7. Operating membrane modules

Operating gas permeation modules is accompanied by various physical effects which may influence the module performance and should be considered when designing gas permeation plants. Fig. 5 depicts these effects.

7.1. Joule–Thomson effect

The permeation of a gas from the pressurized side of a membrane to the unpressurized side can be considered as an isenthalpic decompression of the gas. As the pressure changes due to permeation and the composition of the gas is constant, the temperature has to change. Details on the Joule–Thomson Effect were reported by Coker et al. [60], Gorissen [61], Welsch [62] and Scholz et al. [63]. The Joule–Thomson effect results in significant cooling of both the raw gas on the feed side of the gas permeation module and the gas on the permeate side. The lower temperature in the module influences the thermodynamic behavior of the gas as well as the mass transfer through the membrane [61].

The lower temperature may result in the condensation of gases. The mass transfer of gas molecules through the polymeric membrane materials increases with increasing temperature, while the selectivity decreases with increasing temperature. As permeance decreases with decreasing temperature, a larger membrane area is required to obtain the pipeline purity.

7.2. Pressure losses

Pressure losses in gas permeation modules are common. On both sides of the membrane, pressure losses reduce the driving force of permeation. In general, these pressure losses are small. Nevertheless, pressure losses are pronounced at subambient pressure on the permeate side of the module. A detailed analysis of pressure losses in hollow fiber gas permeation modules was reported by Rautenbach et al. [64] and Scholz et al. [63].

7.3. Concentration polarization

Due to the selective permeation of gas molecules, the retained gas species molecules accumulate at the membrane surface. This phenomenon is referred to as concentration polarization [65–67]. It is highly dependent on the flux of the components through the membrane and the higher the flux, the more pronounced is the concentration polarization. Concentration polarization reduces the mass transfer through the membrane. Both the process selectivity as well as the flux are reduced. Concentration polarization occurs in the porous support of the membrane and in the boundary layers. Details on the effects of concentration polarization can be found in [66,67,63]. The permeances of commercially available membrane materials for CO_2/CH_4 separation are generally moderate so that concentration polarization will not be an issue in biogas upgrading.

7.4. Real gas behavior

Since the biogas is delivered at high pressures to the natural gas grid, the real gas behavior of the gas components has to be

Table 5
Comparison hollow fiber, spiral wound, and envelope type gas permeation modules. Adapted from [59].

	Unit	Hollow fiber	Spiral wound	Envelope
Packing density	m^2/m^3	< 10000	200–1000	30–500
Approximate area per module	m^2	300–600	20–40	5–20
Costs for module	US-\$/m^2	2–10	10–50	50–200
Pretreatment requirements		High	Fair	Minimal

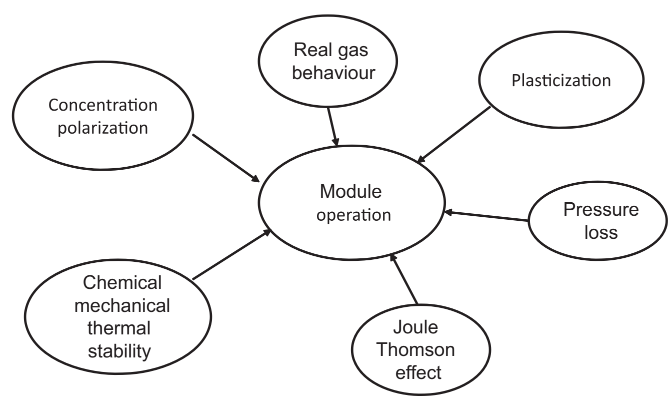


Fig. 5. Various thermodynamic and physical phenomena influencing module performance in the gas permeation process.

Table 6
Comparison of different membrane module designs to be applied to gas permeation.

Supplier	Module type	Polymer
Air Liquide Medal	Hollow fiber	Polyimide, polyaramide
Air products	Hollow fiber	Polysulfone
GMT Membrantechnik	Envelope type	Poly(ethylene oxide)poly(butylene therephthalate)
Evonik	Hollow fiber	Polyimide
IGS Generon Membrane Technology	Hollow fiber	Tetrabrome polycarbonate
Kvaerner Membrane Systems (no longer active)	Spiral wound	Cellulose acetate
MTR Inc.	Spiral wound	Perfluoro polymer, silicone rubber
Parker	Hollow fiber	Polyphenylene oxide
Praxair (no longer active)	Hollow fiber	Polyimide
UBE Membranes	Hollow fiber	Polyimide
UOP former Grace	Spiral wound	Cellulose acetate

taken into account [63]. In particular, CO_2 has a pronounced real gas behavior and the permeation of CO_2 is reduced by real gas behavior. This effect increases with increasing pressure. More information on the influence of real gas behavior on gas permeation can be found in [68].

7.5. Plasticization of polymeric membrane materials

It is a well known fact that high CO_2 partial pressure causes significant sorption of CO_2 in the polymer matrix, translating to increased polymer chain mobility [69–73], which is referred to as plasticization. Thus, the mass transport for all gas species through the membrane is enhanced. Moreover, plasticization significantly reduces the selectivity of the gas permeation material. Hence, it is essential to apply polymers with high selectivities as well as high plasticization resistance.

8. Gas permeation processes

8.1. Driving force generation

In gas permeation, the driving force of permeation is the partial pressure difference Δp_i of the gas components from the feed side to the permeate side:

$$\Delta p_i = x_i \cdot p_F - y_i \cdot p_P. \tag{2}$$

Thus in gas permeation, three different methods can be applied to generate the driving force: feed compression, a vacuum on the permeate side, and the application of a sweep gas on the permeate side. Fig. 6 illustrates these various methods. On the left side of Fig. 6, a gas permeation process is presented in which the feed is compressed and the permeate side operates at ambient pressure. The feed gas which is fed to the gas permeation module remains pressurized as it flows through the module and leaves the module upgraded as retentate stream. Hence, the natural gas pipeline pressure is generated by the compressor, which provides the driving force for permeation.

The central part of Fig. 6 depicts a gas permeation process which applies subambient pressure on the permeate side of the gas permeation module to provide the driving force of permeation. This process configuration is particularly efficient if small amounts of gas have to be removed from the bulk streams and the components to be removed permeate quickly through the membrane. However, the generated pressure ratio is limited, due to a minimum applicable pressure of 0.2 bar [74]. Moreover, the upgraded biogas is not pressurized and an additional compressor is required to supply the gas at natural gas grid pressure.

Using a sweep stream on the permeate side can be used to generate the driving force of permeation, which is shown on the right side of Fig. 6. Here, the permeate stream is diluted, so that the concentration of the fast permeating components is reduced [75]. The raw gas, the product gas, or an inert gas can be used as sweep gas and it has to be chosen carefully as it influences the plant economics. However, using a sweep stream can be inefficient if the permeate is the product since the sweep gas contaminates the permeate stream.

Applying only a sweep gas operation is inappropriate, as only a limited driving force is generated. The maximal applicable driving force by using a sweep gas is

$$\Delta p_i = x_i \cdot p_F - \underbrace{y_i \cdot p_P}_{\approx\, 0}. \tag{3}$$

For sweep gas operation, the last term in Eq. (3) is approximately 0. Hence, the driving force is linearly dependent on the feed pressure. Without applying any pressure on the feed side, the driving force is limited to a mole fraction of the respective gas components in the feed gas. Assuming a pure gas on the feed side at atmospheric pressure, only a driving force of 1 bar is generated. In addition, the feed gas is not pressurized, so this has to be done later, prior to grid injection. However, using a sweep gas in combination with feed gas compression may be beneficial if an appropriate sweep gas is available [75].

Using feed compression may be efficient since then the product gas is already pressurized. However, as the raw gas contains significant quantities of CO_2, it is also compressed and the corresponding energy is lost when the gas permeates through the membrane. To compare the different methods of generating a driving force, the required energy to drive the process has to be evaluated.

Fig. 7 depicts the specific energy demand for a one stage gas permeation process as a function of the CO_2 mole fraction in the feed gas. Here, the feed gas is considered as a binary mixture of CH_4 and CO_2. In order to compare the operation in which subambient pressure on the permeate side is used to the compression of the feed gas, a product CH_4 mole fraction of 96% is specified. The specific energy demand is the ratio of the compressor load P_{el} and the

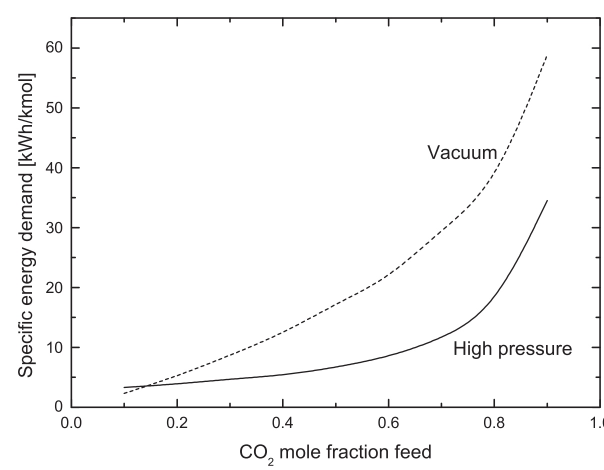


Fig. 7. The specific energy demand is plotted as a function of the mole fraction of CO_2 in the feed gas. A high pressure operation on the feed side with a pressure of 1 bar at the permeate side is compared to using a subambient pressure of 0.2 bar on the permeate side with a feed gas pressure of 1.1 bar.

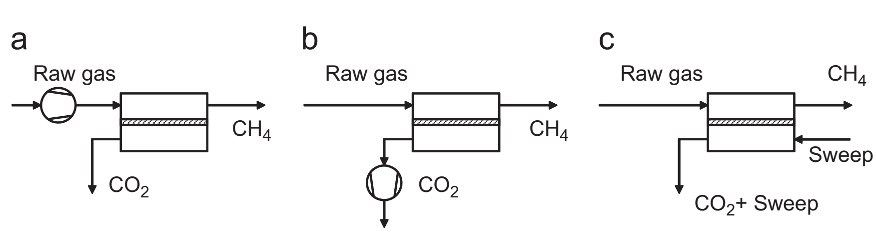


Fig. 6. Driving force generation concepts for gas permeation. In (a) the feed gas is compressed and the product gas is pressurized. In (b) the driving force is generated by applying subambient pressure on the permeate side. Here the product gas has to be compressed for grid injection. In process (c) a sweep stream on the permeate side of the gas permeation module lowers the concentration of the fast permeating components and thus generates the driving force.

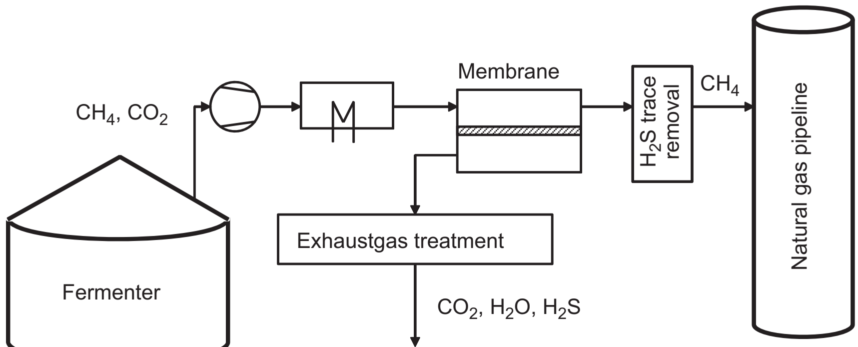


Fig. 8. The process equipment for a membrane-based upgrading process. The raw gas leaving the fermenter is pressurized up to the grid pressure by a multistage compressor using interstage cooling. Subsequently, the gas temperature is controlled in a heat exchanger to protect the gas permeation membrane from high temperatures. In the gas permeation system, the raw gas is split into a CO_2 rich stream which is referred to as the permeate, and a CH_4 rich stream, which is the retentate. The permeate stream is fed to an exhaust gas treatment unit which captures the components not to be fed to the environment.

product flow rate $\dot{n}_{\text{product}}$,

$$\text{specific energy demand} = \frac{P_{\text{el}}}{\dot{n}_{\text{product}}}. \quad (4)$$

The compressor efficiency is assumed to be 0.72. If subambient pressure on the permeate side is applied, the pressure is assumed to be 0.2 bar and the feed pressure is assumed to be 1.1 bar. When compression of the feed side is applied to generate the driving force, the feed pressure in the gas permeation module is 16 bars. In both cases, the pressure losses of the membrane module are neglected as the pressure losses are low [63]. The permeate pressure is fixed at an ambient pressure of 1 bar.

Fig. 7 shows that applying subambient pressure on the permeate side is favorable for CO_2 mole fractions in the feed of less than 15%. If the CO_2 mole fraction is higher than 15%, feed compression should be applied. For both a subambient pressure on the permeate side and applying high pressures on the feed side, the specific energy demand strongly increases with increasing CO_2 load in the feed gas. Concerning biogas upgrading, in which the feed gas typically consists of 30–50% CO_2, compression of the feed gas is beneficial.

In conclusion, when upgrading biogases containing CO_2 mole fractions of more than 20% feed gas, compression should be applied. However, this is a rough estimate and should be used only as an indicator. Three aspects have been neglected. First, a membrane-based biogas upgrading process would not consist of a single stage process, as CH_4 losses are pronounced and strongly degrade the economic efficiency of the process. Second, the compressors are modeled as one stage compressors without interstage cooling. Normally, a three stage compressor with interstage cooling would be applied if the gas is to be pressurized up to 16 bar. Biegler et al. [76] gave a rule of thumb for determining the number of compressor stages N:

$$\frac{P_k}{P_{k-1}} = \left(\frac{P_n}{P_0}\right)^{1/N}. \quad (5)$$

Here, P_k/P_{k-1} is the pressure ratio per compression stage, which ranges typically between 1.15:1 and 4:1 (see Table 7) and P_n/P_0 is the pressure ratio for the whole compression process. Third, using subambient pressure on the permeate side delivers the product gas at 1.1 bar. Hence, an additional compressor has to supply the pressure to inject the gas into the natural gas grid.

8.2. Process equipment

By upgrading biogas using gas permeation modules, at least four process steps are required, using as equipment: the compression equipment, the membrane modules, a heat exchanger upstream of the gas permeation modules, and the off gas treatment. The membrane modules have explicitly been described in Section 6.

Table 7
Comparison of various compressors which could be applied for generating the driving force. These compressors are evaluated in terms of pressure level, flow rate, and resistance against acidic gases. Adapted from [77].

	Axial	Centrifugal	Reciprocal
Pressure 25 bar	–	+	+
Flow rate 100−2000 m^3/h	+	−	+
Pressure ratio	1.15:1	1.7:1–3.1:1	3:1–4:1
Particle tolerance	−	−	−
Liquid tolerance	−	−	−
Changes in gas composition	−	−	+
Efficiency	Up to 90%	0.83%	80%–92%
Appropriate for biogas	−	−	+

8.2.1. Compression equipment

There are various types of compressors for generating the driving force: axial compressors, centrifugal compressors, and reciprocal compressors. These compressors are frequently applied in the process industry as well as in the energy generation industry. However, the applications of these compressors are limited by the pressure level to be generated and by the volume stream to be compressed. As the process conditions may be harsh, due to elevated H_2S and H_2O concentrations at high pressures, the compressors have to be resistant to the gases which are compressed.

Table 7 summarizes the criteria which have to be met by the compression equipment in order to compress a raw biogas stream. Typical raw gas flow rates of industrial scale biogas upgrading plants range from 100 m^3/h to 2000 m^3/h.

8.2.2. Heat exchanger

A heat exchanger is required to control the gas temperature at the gas permeation module inlet. Due to the compression of the gas prior to the membrane system, the gas temperature increases significantly and hence the membranes have to be protected against high temperatures. In general, both plate heat exchangers as well as shell and tube heat exchangers can be used. Due to the higher packing density and the application at high pressures of more than 20 bar, it is recommended to use a shell and tube heat exchanger in biogas upgrading.

8.2.3. Off gas treatment

The exhaust gas leaving the membrane-based biogas upgrading system consists mainly of CO_2. However, significant amounts

of H_2S, H_2O, and CH_4 are present in the off gas, which cannot be fed to the ambient. The off gas has to meet strict environmental standards [5] and particularly, the CH_4 content has to be reduced.

The CH_4 content in the off gas determines the selection of the appropriate exhaust gas treatment method. At low CH_4 concentration ($<2\%$), a thermal oxidation can be applied to reduce the CH_4 content [5]. At low CH_4 concentrations, the combustion has to be supported by a combustible gas. At elevated CH_4 (2–6%) concentrations, either a thermal or a catalytic oxidation can be used.

Various tailor-made burners have recently been developed, e.g., the FLOX®-burner and the catalytic combustion system ZETECH4® (CarboTech, Germany) [5]. For driving the FLOX®-burner (e-flox GmbH, Germany), a CH_4 concentration of more than 7% is required. At low CH_4 concentration, of less than 0.4%, the recuperative and the catalytic burner of Caverion (Caverion GmbH, Germany) is able to reduce the CH_4 content.

8.3. Single stage gas permeation processes for biogas upgrading

Fig. 9 illustrates two single stage gas permeation processes for upgrading biogas. The process on the left hand side is the most simple gas permeation process to remove CO_2 from CH_4. However, the CH_4 losses applying this process are high and determined by selectivity. The process on the right side shows a single stage process with a partial recycling of the permeate stream. Applying this process, the CH_4 recovery increases significantly [57]. Nevertheless, the CH_4 recovery is limited and cannot reach values of more than 95% if a CH_4 purity of 96% has to be achieved. In addition, the partial recycling of the permeate stream drastically increases the flow rate through the compressor and hence increases the energy demand for driving the separation process. Details on single stage processes were investigated by Jaeschke and Ajhar [49].

Fig. 10 illustrates the tradeoff between CH_4 recovery and CH_4 purity. Here, the CH_4 purity is plotted as a function of CH_4 recovery for CO_2/CH_4 selectivities ranging from 20 to 100. The CH_4 product mole fraction increases with decreasing CH_4 recovery. However, the separation performance is dependent on the membranes selectivity. The higher the selectivity, the higher the CH_4 product mole fraction for a specific CH_4 recovery. If a CH_4 recovery of 96% is considered, the CH_4 mole fraction in the retentate is 66% for a selectivity of 20 and 79% for a selectivity of 40. However, for 96% CH_4 recovery, the CH_4 product mole fraction is 91% for a selectivity of 80 and 93% for a selectivity of 100. Thus, the effect of membrane selectivity is less pronounced when high selectivities are considered. Today, commercially available membrane materials have CO_2/CH_4 selectivities of about 20 [28]. Furthermore, to take advantage of highly selective membranes, high pressure ratios have to be provided which is energy demanding [78]. Hence, membranes with selectivities of more than 100 cannot efficiently be applied.

The permeate mole fraction of CO_2 depends on the pressure ratio, which is the ratio of the feed pressure p_F to the permeate pressure p_P,

$$\phi = \frac{p_F}{p_P}. \tag{6}$$

Fig. 11 shows the mole fraction of CO_2 as a function of the applied pressure ratio. The simulations were performed for a binary mixture of CO_2 and CH_4 with mole fraction of 50/50. The permeate pressure is 1 bar and the retentate purity of CH_4 is fixed at 96%. The dashed lines in Fig. 11 depict the interface between the regime in which the gas permeation process is selectivity controlled and the region where the pressure ratio most significantly influences the CO_2 mole fraction in the permeate. This interface between the two regions is specified by 90% of the permeate mole fraction of CO_2 at an infinite pressure ratio which can be determined by [65]

$$y_{CO_2} = \frac{\alpha x_{CO_2}}{1 - x_{CO_2} + \alpha x_{CO_2}} \quad \text{at } (\phi = \infty). \tag{7}$$

Here, x_{CO_2} is the CO_2 mole fraction on the feed side of the gas permeation module and α the ideal separation factor. In Table 8 these values are determined for various CO_2/CH_4 selectivities.

For biogas upgrading, where pressure ratios of more than 16 and selectivities of more than 40 are used, it is likely that the gas permeation modules operate in the selectivity controlled region. However, applying single stage gas permeation processes is inefficient, due to significant CH_4 losses. Multistage gas permeation processes can be applied to tackle this drawback.

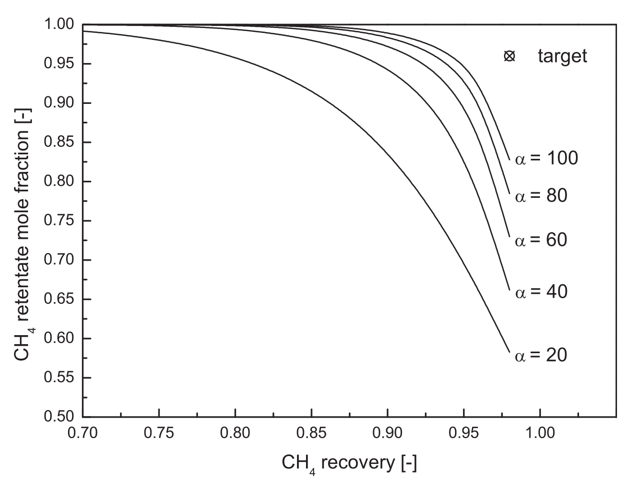


Fig. 10. Trade off between CH_4 purity and CH_4 recovery for the separation of 50% CO_2 and 50% CH_4. The curves are presented for CO_2/CH_4 selectivities ranging from 20 to 100. The target value for biogas upgrading is illustrated.

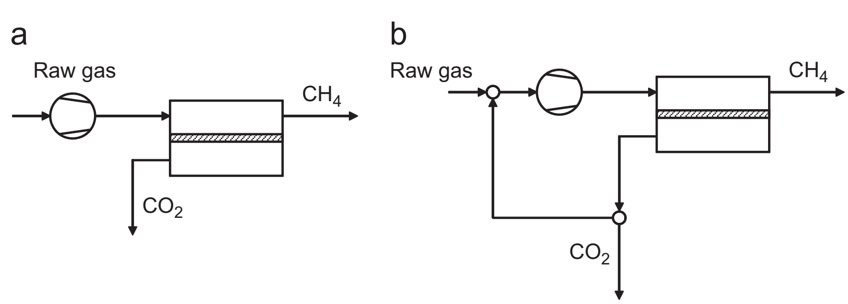


Fig. 9. Single stage membrane-based biogas upgrading process using feed compression. Process (a) the permeate flows to the ambient. Process (b) the permeate is partially recycled to enhance the CH_4 recovery.

8.4. Multistage processes

Applying various membrane modules in a multistage system is a strategy to obtain high product purity and simultaneously increase the CH_4 recovery of the upgrading system. Fig. 12 depicts four different two stage upgrading processes.

In process (a), the first module removes CO_2 from the raw biogas gas. However, the CH_4 purity of the gas leaving the first gas permeation stage is lower than the required CH_4 purity for grid injection. In order to purify the CH_4 stream, a second membrane module is applied, which controls the product purity. However, the permeate stream of the second gas permeation module contains significant amounts of CH_4 and this stream is recycled to enhance the CH_4 recovery.

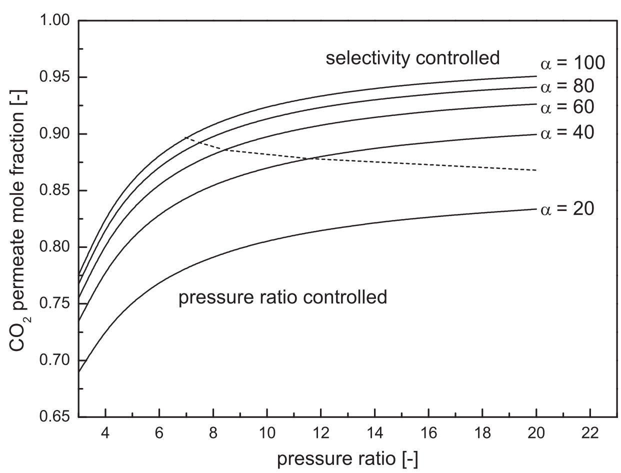


Fig. 11. Permeate mole fraction of CO_2 as a function of pressure ratio for selectivities ranging from 20 to 100. The dashed line specifies the interface between the regions where the operation is selectivity controlled and where pressure ratio controlled.

Table 8
Calculation of the maximal CO_2 mole fraction in the permeate at an infinite pressure ratio. 90% of the maximal value indicate the interface between the pressure ratio controlled regime and the selectivity controlled regime.

Selectivity	Max. CO_2	90% of max. CO_2
20	0.952	0.857
40	0.976	0.878
60	0.984	0.885
80	0.988	0.889
100	0.990	0.891

In process (b), which was investigated by Deng and Hägg [6], the required CH_4 purity is obtained in one step. However, significant amounts of CH_4 permeate through the membrane and a second gas permeation module is applied to recover it. A second compressor is required to generate the driving force of permeation for the second gas permeation module. The CH_4 rich stream of the second module is recycled in front of the first stage compressor and is mixed with the raw gas.

Process (c) is related to process (b) [6]. Here, the CH_4 rich stream obtained from the second membrane stage is purified to meet the required purity for grid injection. This stream is mixed with the CH_4 rich stream from the first stage.

In process (d) both using a sweep stream as well as compressing the raw gas are applied to generate the driving force of permeation. Here, the raw biogas is used as a sweep gas to increase the driving force in the second membrane module. This process design is similar to that of process (a). The application of the sweep stream is only useful if the CO_2 mole fraction of the permeate of the second module is higher than the CO_2 mole fraction of the feed stream. Hence, the sweep gas reduces the CO_2 mole fraction on the permeate side of the second module. The driving force increases and less membrane area is required.

Fig. 13 shows a three stage biogas upgrading process [79]. This process is similar to process (d) in Fig. 12. The unpressurized raw gas is mixed with the permeate of module 3. It is important that mixing the raw gas stream with the permeate improves the process by diluting the permeate stream of module 2. Accordingly, less membrane area is required without increasing the recycle stream.

In Fig. 14 a three stage membrane process is shown which was recently patented by Evonik Industries [81]. In this process polymeric membranes are applied which have CO_2/CH_4 selectivities of more than 50. In the first stage the bulk of CO_2 is removed from CH_4. The retentate of the first stage is fed to a second stage in which the final CH_4 purity is adjusted. The permeate of the second stage contains significant amounts of CH_4. To increase the CH_4 recovery the permeate stream is recycled and mixed with the raw gas stream. In order to further increase the CH_4 recovery the permeate of the first stage which contains only a small fraction of CH_4 is fed to a third gas permeation stage. Here, the CO_2 permeates through the membrane and it leaves the process as exhaust gas. The retentate stream which is enriched in CH_4 is recycled and mixed with raw gas stream. The driving

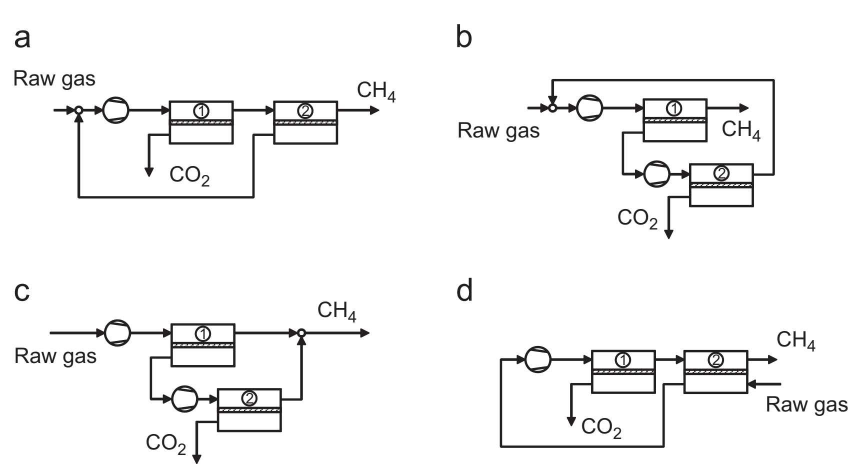


Fig. 12. Two stage processes for biogas upgrading. In process (a) only one compressor is required and the permeate of the second stage is recycled. Process (b) requires two compressors and the retentate of the second stage is recycled. In process (c) two compressors are required and the retentate of the second stage is mixed with the retentate of the first stage. In process (d) the feed gas is used as a sweep gas on the permeate side of the second module. Here only one compressor is required.

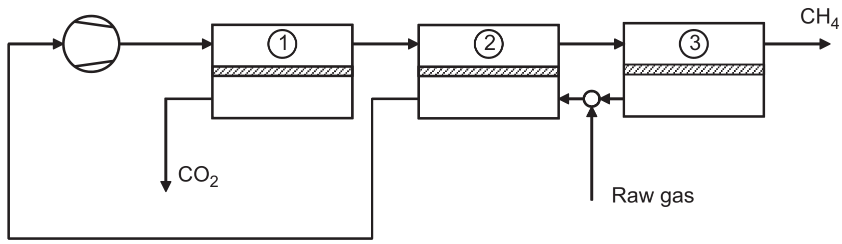


Fig. 13. Flowsheet of a three stage gas permeation process proposed by Makaruk and Harasek [79]. Here, the feed is used as a sweep gas to increase the driving force by mixing the permeate of the third module and the raw gas.

Table 9
Various gas permeation upgrading processes are compared in terms of energy demand, CH_4 recovery, required membrane area, and specific upgrading costs. Permeance of CO_2 66.67 GPU; Permeance of CH_4 2.08 GPU.

	CH_4 recovery	Specific energy (kW h/m^3)	Specific area (m^2 h/m^3)	Upgrading costs (Euro ct h/m^3)	Supply pressure (bar)	Ref.
Single stage	0.855	0.277	1.70	0.228	20	[6]
Two stage (Fig. 12 process (a))	0.957	0.318	1.92	0.220	20	[6]
Two stage (Fig. 12 process (b))	0.997	0.286	1.69	0.201	20	[6]
Two stage (Fig. 12 process (c))	0.973	0.295	1.57	0.206	20	[6]

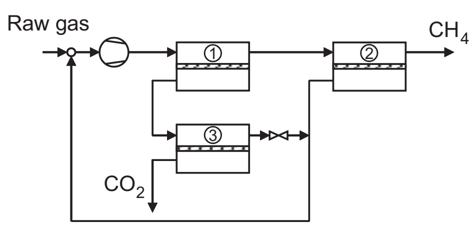


Fig. 14. Hybrid processes for biogas upgrading. (a) depicts a hybrid process in which the membrane removes the bulk of CO_2 and the conventional process equipment further polishes the gas stream. In (b) the conventional gas separation equipment is used to recover the CH_4 lost in the permeate of the membrane stage.

force for permeation in the third membrane stage is generated by a pressure control valve which adjusts the pressure on the permeate side of the first stage and the pressure on the feed side of the third stage simultaneously.

By applying this process CH_4 recoveries of more than 99% can be obtained while the CH_4 purity is higher than 96 %. The high CH_4 recovery is generally obtained on cost of the increased recycle stream. However, an increased membrane selectivity reduces the recycle stream. In fact this process is momentarily commercialized by several companies (EnviTec Biogas AG, MT-BioMethan GmbH) and process data such as specific energy demand for industrial size upgrading plants based on the three stage membrane configuration will be available soon. Thus we will not include it in the following evaluation (see Table 9).

Table 9 evaluates the various multistage processes in terms of CH_4 recovery, specific energy demand, specific membrane area requirement, as well as in terms of specific upgrading costs. Process (b) from Fig. 12 has the lowest upgrading costs and the highest CH_4 recovery. Compared to conventional process technology presented in Table 3 the membrane processes consume slightly more energy than the conventional processes. The specific upgrading costs are higher than the upgrading costs for conventional upgrading equipment. Nevertheless, using a membrane system the product gas is supplied at natural gas grid pressure so that no additional compression is required. In conventional processes, the gas is supplied at low to moderate pressure. Thus, the energy and the costs for compression to grid pressure are not included in the specific energy demand and the upgrading costs. Therefore, the total upgrading costs including the compression to grid pressure should be used to compare the different technologies and thus membrane-based systems become more attractive.

8.5. Hybrid processes

Gas permeation processes are quite efficient for moderate purification of gases [37]. To obtain high purity products from a gas permeation module requires either a large membrane or strong driving forces, which translates to significant operational costs. Hybrid processes in which membrane technology is combined with conventional gas separation equipment may be superior to the individual processes in which only one single technology (i.e., amine scrubbing, membrane technology) is applied [28].

Fig. 14 illustrates two hybrid processes for biogas upgrading. In process (a), the gas permeation module is used to perform the bulk separation of CO_2 and CH_4 so that only moderate CH_4 purities are obtained from the membrane module. The conventional process equipment downstream of the gas permeation module polishes the CH_4 stream. Two exhaust gas streams enriched in CO_2 are generated.

In process (b), the gas permeation module is applied to obtain the CH_4 purity in a single membrane stage. However, as demonstrated in Section 8.3, the permeate stream contains significant quantities of CH_4, which should be recovered. The permeate stream from the membrane stage flows to the conventional gas separation equipment. Here, the size of the equipment is small, as the permeate stream is generally less than 50% of the raw gas stream. The recovered CH_4 can be pressurized and mixed with the product from the gas permeation module.

8.6. Upgrading combined with utilization in combined heat and power engines

Gas permeation processes can be linked efficiently with combined heat and power engines [80]. Here, the permeate of the membrane stage contains CH_4 for driving the combined heat and power engine. This option is quite promising, as the heat generated at the engine can be used efficiently for heating the fermentation process. A detailed investigation of such a process was recently carried out by Makaruk et al. [80].

Table 10
Installed membrane-based biogas upgrading plants.

Country	Location	Operating since	Product stream (m^3/h)
The Netherlands	Collendoorn	1990	25 (today 375)
The Netherlands	Beverwijk	2006	80
US	Raeger (PA)	2006	4721[a]
US	Johnson City (TN)	2006	2361[a]
Austria	Bruck an der Leitha	2007	100
US	Kersey (PA)	2007	14,164[a]
US	Imperial (PA)	2007	7082[a]
US	Cairnbrook (PA)	2007	4721[a]
US	Davidsville (PA)	2007	2361[a]
US	Oklahoma City (OK)	2008	2361[a]
US	Church Hill (TN)	2008	2361[a]
US	Winder (GA)	2008	7082[a]
US	Atlanta (GA)	2009	8263[a]
US	Seattle (WA)	2009	18,886[a]
Germany	Kisslegg–Rahmhaus	2010	300
The Netherlands	Witteveen	2010	200
US	Pittburgh (PA)	2010	4721[a]
US	New Orleans (LA)	2010	10,623[a]
Austria	Wiener Neustadt	2011	120
Austria	Neunkirchen	2011	10
US	Athens (TN)	2011	3541[a]
US	San Diego (CA)	2011	2361[a]
US	Fresno (CA)	2011	2361[a]
Norway	Lillehammer	2012	30

[a] Raw gas flow rate.

9. Installed membrane-based biogas plants

Although membranes show remarkable performance in upgrading biogas, only a limited number of membrane-based upgrading plants have been installed. Table 10 describes the plants which have been installed in the last few years in Europe and the US. In principle, two categories of biogas upgrading plants are distinguished: commercial plants and plants installed for research.

9.1. Membrane-based upgrading plants in research and development

In 1989, Rautenbach and Welsch [46,81] constructed a biogas upgrading plant which operated for more than two years at a landfill in Germany. The flow rate of the raw gas was 200 m^3(STP)/h and the gas was supplied to the natural gas grid at 35 bar. Polyimide hollow fiber modules (UBE Industries) with an area of 700 m^2 were installed. They analyzed various multistage processes and identified a two stage cascade with a recycle of the second step permeate as a simple and reliable upgrading process (see Fig. 12 process (a)). In addition, they analyzed the influence of the Joule–Thomson effect on the permeation performance.

Stern et al. [48] built a membrane-based biogas upgrading plant which was installed to upgrade gas generated by a municipal waste water treatment plant. The flow rate was 3.4 m^3(STP)/h and the CH_4 mole fraction of the feed gas was 63% balanced with CO_2 and small amounts of organic compounds. However, the raw gas was compressed to 55 bar to supply both the pressure to drive the separation process and the required grid pressure. A single stage process was implemented, to investigate the separation performance of the gas permeation modules.

Makaruk and Harasek [80,82] presented experimental results from a gas permeation plant which produces natural gas substitute for utilization as fuel gas and for grid injection. A two stage membrane cascade was installed with recycling of the second stage permeate (see Fig. 12 (a)). The upgrading plant produces 100 m^3(STP)/h with a methane purity of 98%.

9.2. Commercial membrane-based upgrading plants

In Europe only a limited number of membrane-based biogas upgrading plants exist. Recently, some plants were installed using polymeric membrane materials. In the US, various membrane-based upgrading plants were installed by Air Liquide. Here, a short overview of the existing plants is given.

The first commercial gas-permeation based biogas upgrading facility in Europe was installed in 1990 in Collendoorn (The Netherlands). Here, the raw gas is produced from a landfill and 25 m^3(STP)/h are injected into the natural gas grid. Hollow fiber membranes (Cirmac) produce a moderate methane purity of 88%.

In 2010, Bebra Biogas installed a two stage biogas plant in Kisslegg-Rahmhaus (Germany) with a capacity of 300 m^3(STP)/h upgraded biogas. A CH_4 purity of 98.7% is achieved and the plant operates at feed pressures of 5–7 bar. The CH_4 mole fraction in the permeate ranges between 3% and 8%. Prior to the gas permeation stage, the gas is dehydrated by condensation and the H_2S is removed by activated carbon. Two stage compression equipment is installed.

In the US, the first membrane-based upgrading plant was installed in 1993 at a landfill in Los Angeles County with a capacity of 2600 m^3/h raw gas. The product gas is used as fuel and has a methane purity of 97.5%. The membranes were provided by UOP (Separex^{TM}).

10. Future perspectives

We expect that membrane-based biogas upgrading will be frequently used as a future upgrading technology due to the following facts.

- An enhanced acceptance of membrane technology by biogas users, plant designers, and gas suppliers, caused by the currently installed reference plants.
- Easy and robust operation as well as the energy efficiency of the gas permeation system.
- High CH_4 recoveries, of more than 99.5%.
- Improved membrane materials with selectivities higher than 60 and adequate permeances.
- Exploration of the biogas upgrading market for small upgrading plants ($<$ 100 m^3(STP)/h) where membrane-based biogas upgrading is particularly efficient.
- The general trend to exchange combined heat and power engines by upgrading equipment.
- The great potential of biogas utilization in India [83–87] and Brazil [88–90].

Research challenges in membrane-based biogas upgrading include the following:

- Stability against minor components like H_2S.
- Plasticization of polymeric membrane materials at elevated CO_2 partial pressures.

11. Conclusions

In this current study concepts for membrane-based biogas upgrading processes are presented. The biogas upgrading process as well as conventional upgrading processes and their characteristics are presented as a benchmark for the membrane process. Gas permeation processes have outstanding properties which make them superior to conventional gas separation equipment in biogas upgrading. However, single stage membrane processes are not able to upgrade the raw biogas economically and limits of the gas

permeation process are discussed in detail. Nevertheless, the typical tradeoff between product gas purity and methane recovery can be dismantled by applying multistage gas permeation networks. Here, high methane purities as well as high methane recoveries can be realized.

The increased application of membrane-based biogas upgrading in the future is expected. The development of polymeric membrane materials which are easy to manufacture and have high CO_2/CH_4 selectivities will fuel the application of gas permeation membranes. In addition, many small scale on-farm combined heat and power engines will be exchanged by biogas upgrading equipment as the generated heat cannot be used efficiently. Ultimately, gas permeation systems are an excellent technology to upgrade biogas as the upgraded gas is delivered at natural gas grid pressure and no additives are required to purify the raw gas.

References

[1] Pielke R, Wigley T, Green C. Dangerous assumptions. Nature 2008;452(7187): 531–2.
[2] Weiland P. Biogas production: current state and perspectivesApplied Microbiology and Biotechnology 2010;85(4):849–60.
[3] Petersson A, Wellinger A. Biogas upgrading technologies—developments and innovations. IEA-Task 2009;37:20.
[4] Bley T, Kirsten C, Weitze M. Bioenergie in Deutschland. Biotechnologische Energieumwandlung 2009:13–35.
[5] Weidner GKLHE, Urban W. Technologien und Kosten der Biogasaufbereitung und Einspeisung in das Erdgasnetz. Ergebnisse der Markterhebung 2007–2008. Technical report; 2008.
[6] Deng L, Hägg M. Techno-economic evaluation of biogas upgrading process using CO_2 facilitated transport membrane. International Journal of Greenhouse Gas Control. 2010;4(4):638–646, http://dx.doi.org/10.1016/j.ijggc.2009.12.013.
[7] Markard J, Stadelmann M, Truffer B. Prospective analysis of technological innovation systems: identifying technological and organizational development options for biogas in SwitzerlandResearch Policy 2009;38(4):655–67.
[8] Ross J, Van Keulen A, Hegarty M, Seshan K. The catalytic conversion of natural gas to useful products. Catalysis Today 1996;30(1–3):193–9.
[9] Raven R, Gregersen K. Biogas plants in Denmark: successes and setbacksRenewable and Sustainable Energy Reviews 2007;11(1):116–32.
[10] PAF Hofmann. Einspeisung von biogas in das erdgasnetz. Technical report 2006.
[11] Anderson C. Landfill gas upgrading to pipeline quality in the US; 2011.
[12] Resch G, Held A, Faber T, Panzer C, Toro F, Haas R. Potentials and prospects for renewable energies at global scale. Energy Policy 2008;36(11):4048–56.
[13] Moriarty P, Honnery D. What is the global potential for renewable energy? Renewable and Sustainable Energy Reviews 2012;16(1):244–52, http://dx.doi.org/10.1016/j.rser.2011.07.151.
[14] McKendry P. Energy production from biomass (Part 1): overview of biomass-Bioresource Technology 2002;83(1):37–46.
[15] Jess A. What might be the energy demand and energy mix to reconcile the world's pursuit of welfare and happiness with the necessity to preserve the integrity of the biosphere? Energy Policy 2010;38(8):4663–78.
[16] Holm-Nielsen J, Al Seadi T, Oleskowicz-Popiel P. The future of anaerobic digestion and biogas utilization. Bioresource Technology 2009;100(22): 5478–84.
[17] Sumathi S, Chai S, Mohamed A. Utilization of oil palm as a source of renewable energy in Malaysia. Renewable and Sustainable Energy Reviews 2008;12(9):2404–21.
[18] Akinbami J, Ilori M, Oyebisi T, Akinwumi I, Adeoti O. Biogas energy use in Nigeria: current status, future prospects and policy implicationsRenewable and Sustainable Energy Reviews 2001;5(1):97–112.
[19] Arthur R, Baidoo M, Antwi E. Biogas as a potential renewable energy source: a Ghanaian case study, Renewable Energy. 2011;36(5):1510–1516, http://dx.doi.org/10.1016/j.renene.2010.11.012.
[20] Berglund M, Borjesson P. Assessment of energy performance in the life-cycle of biogas production. Biomass and Bioenergy 2006;30(3):254–66.
[21] Poschl M, Ward S, Owende P. Evaluation of energy efficiency of various biogas production and utilization pathways. Applied Energy 2010;87(11): 3305–21.
[22] Rasi S, Veijanen A, Rintala J. Trace compounds of biogas from different biogas production plants. Energy 2007;32(8):1375–80.
[23] Rasi S, Läntelä J, Rintala J. Trace compounds affecting biogas energy utilisation—a review. Energy Conversion and Management 2011;52(12): 3369–75.
[24] Patterson T, Esteves S, Dinsdale R, Guwy A. An evaluation of the policy and techno-economic factors affecting the potential for biogas upgrading for transport fuel use in the UK. Energy Policy. 2011;39(3):1806–1816, http://dx.doi.org/10.1016/j.enpol.2011.01.017.
[25] DVGW-Arbeitsblatt G, 262 nutzu ng von gasen aus regenerativen quellen in der öffentlichen gasversorgung, Stand November.
[26] des Gas D. und wasserfaches ev (dvgw): Arbeitsblatt g 260 gasbeschaffenheit; 2000.
[27] Foss M, Head C. Interstate natural gas—quality specifications & interchangeability. Center for Energy Economics, Bureau of Economic Geology, University of Texas at Austin, December 2004.
[28] Baker R, Lokhandwala K. Natural gas processing with membranes: an overviewIndustrial & Engineering Chemistry Research 2008;47(7):2109–21.
[29] Yang H, Xu Z, Fan M, Gupta R, Slimane R, Bland A, et al. Progress in carbon dioxide separation and capture: a reviewJournal of Environmental Sciences 2008;20(1):14–27.
[30] Cavenati S, Grande C, Rodrigues A, Kiener C, Muller U. Metal organic framework adsorbent for biogas upgrading. Industrial & Engineering Chemistry Research 2008;47(16):6333–5.
[31] Grande C, Rodrigues A. Layered vacuum pressure—swing adsorption for biogas upgrading. Industrial & Engineering Chemistry Research 2007;46(23): 7844–8.
[32] Alonso-Vicario A, Ochoa-Gómez J, Gil-Río S, Gómez-Jiménez-Aberasturi O, Ramírez-López C, Torrecilla-Soria J, et al. Purification and upgrading of biogas by pressure swing adsorption on synthetic and natural zeolites. Microporous and Mesoporous Materials 2010;134(1–3):100–7.
[33] Waldo R, Burkinshaw J. Distillation plus membrane processing of gas streams. US Patent 4,936,887; June 26, 1990.
[34] Göttlicher G, Pruschek R. Comparison of CO_2 removal systems for fossil-fuelled power plant processes. Energy Conversion and Management 1997;38: S173–8.
[35] Ryckebosch E. Drouillon M, Vervaeren H. Techniques for transformation of biogas to biomethane. Biomass and Bioenergy 2011;35(5):1633–1645, http://dx.doi.org/10.1016/j.biombioe.2011.02.033.
[36] Tessendorf S, Gani R, Michelsen M. Modeling, simulation and optimization of membrane-based gas separation systems. Chemical Engineering Science 1999;54(7):943–55.
[37] Bhide B, Voskericyan A, Stern S. Hybrid processes for the removal of acid gases from natural gas. Journal of Membrane Science 1998;140(1):27–49.
[38] Hao J, Rice P, Stern S. Upgrading low-quality natural gas with H_2S- and CO_2-selective polymer membranes. Part I. Process design and economics of membrane stages without recycle streams. Journal of Membrane Science 2002;209(1):177–206.
[39] Baker R. Future directions of membrane gas-separation technology. Membrane Technology 2001;2001(138):5–10.
[40] Lokhandwala K, Pinnau I, He Z, Amo K, DaCosta A, Wijmans J, et al. Membrane separation of nitrogen from natural gas: a case study from membrane synthesis to commercial deploymentJournal of Membrane Science 2010;346(2):270–9.
[41] Chinn D, Okeowo S, Euhus J, Husain S. Process for upgrading natural gas with improved management of CO_2. US Patent Application 12/361,961; 2009.
[42] Brinkmann T, Wind J, Ohlrogge K. Membranverfahren in der Erdgasaufbereitung. Chemieingenieurtechnik 2003;75(11):1607–11.
[43] Harasimowicz M, Orluk P, Zakrzewska-Trznadel G, Chmielewski A. Application of polyimide membranes for biogas purification and enrichment. Journal of Hazardous Materials 2007;144(3):698–702.
[44] Kimura S, Walmet G. Fuel gas purification with permselective membranes. Separation Science and Technology 1980;15(4):1115–33.
[45] Qiu M, Hwang S, Kao Y. Economic evaluation of gas membrane separator designs. Industrial & Engineering Chemistry Research 1989;28(11): 1670–1677.
[46] Rautenbach R, Welsch K. Treatment of landfill gas by gas permeation—pilot plant results and comparison to alternatives. Desalination 1993;90(1–3):193–207.
[47] Rautenbach R, Dahm W. Gas permeation—module design and arrangement. Chemical Engineering and Processing 1987;21(3):141–50.
[48] Stern S, Krishnakumar B, Charati S, Amato W, Friedman A, Fuess D. Performance of a bench-scale membrane pilot plant for the upgrading of biogas in a wastewater treatment plant. Journal of Membrane Science 1998;151(1):63–74.
[49] Jäschke S. Evaluierung der Gaspermeation zur Einspeisung von Biogas ins Erdgasnetz. Diploma thesis, RWTH Aachen University 2006.
[50] Simons K, Nijmeijer K, Wessling M. Gas–liquid membrane contactors for CO_2 removal. Journal of Membrane Science 2009;340(1–2):214–20.
[51] Marzouk S, Al-Marzouqi M, El-Naas M, Abdullatif N, Ismail Z. Removal of carbon dioxide from pressurized CO_2–CH_4 gas mixture using hollow fiber membrane contactors. Journal of Membrane Science. 2010;351(1–2):21–27, http://dx.doi.org/10.1016/j.memsci.2010.01.023.
[52] Faiz R, Al-Marzouqi M. Mathematical modeling for the simultaneous absorption of CO_2 and H_2S using MEA in hollow fiber membrane contactors. Journal of Membrane Science 2009;342(1–2):269–78.
[53] Basu S, Khan A, Cano-Odena A, Liu C, Vankelecom I. Membrane-based technologies for biogas separations. Chemical Society Reviews 2009;39(2): 750–68.
[54] Li S, Martinek J, Falconer J, Noble R, Gardner T. High-pressure CO_2/CH_4 separation using SAPO-34 membranes. Industrial & Engineering Chemistry Research 2005;44(9):3220–8.
[55] Li S, Falconer J, Noble R, Krishna R. Modeling permeation of CO_2/CH_4, CO_2/N_2, and N_2/CH_4 mixtures across SAPO-34 membrane with the Maxwell–Stefan equations. Industrial & Engineering Chemistry Research 2007;46(12): 3904–11.

[56] Li S, Carreon M, Zhang Y, Funke H, Noble R, Falconer J. Scale-up of SAPO-34 membranes for CO_2/CH_4 separation. Journal of Membrane Science. 2010;352(1–2):7–13, http://dx.doi.org/10.1016/j.memsci.2010.01.037.
[57] Jäschke S, Ajhar M, Melin T. Evaluierung der Gaspermeation zur Einspeisung von Biogas ins Erdgasnetz. Energie, Wasser-Praxis.
[58] Scholz M, Wessling M, Balster J. Design of membrane modules for gas separations, Copyright Year: chapter 5, 2011, ISBN: 978-1-84973-347-2.
[59] Drioli E, Giorno L. Comprehensive membrane science and engineering. Elsevier Science; 2010.
[60] Coker D, Allen T, Freeman B, Fleming G. Nonisothermal model for gas separation hollow-fiber membranes. AIChE Journal 1999;45(7):1451–68.
[61] Gorissen H. Temperature changes involved in membrane gas separations. Chemical Engineering and Processing 1987;22(2):63–7.
[62] Welsch K. Gaspermeation—membranwerkstoffe, stofftransport und anwendungsbeispiele. PhD thesis, RWTH Aachen University; 1992.
[63] Scholz M, Harlacher T, Melin T, Wessling M. Modeling gas permeation by linking non-ideal effects. Industrial & Engineering Chemistry Research, http://dx.doi.org/10.1021/ie202689m.
[64] Rautenbach R, Struck A, Roks M. A variation in fiber properties affects the performance of defect-free hollow fiber membrane modules for air separation. Journal of Membrane Science 1998;150(1):31–41.
[65] Melin T, Rautenbach R. Membranverfahren. Springer; 2004.
[66] Mourgues A, Sanchez J. Theoretical analysis of concentration polarization in membrane modules for gas separation with feed inside the hollow-fibers. Journal of Membrane Science 2005;252(1–2):133–44.
[67] Baker R, Wijmans J, Athayde A, Daniels R, Ly J, Le M. The effect of concentration polarization on the separation of volatile organic compounds from water by pervaporation. Journal of Membrane Science 1997;137(1–2): 159–72.
[68] Alpers A, Keil B, Ludtke O, Ohlrogge K. Organic vapor separation: process design with regards to high-flux membranes and the dependence on real gas behavior at high pressure applicationsIndustrial & Engineering Chemistry Research 1999;38(10):3754–60.
[69] Visser T, Masetto N, Wessling M. Materials dependence of mixed gas plasticization behavior in asymmetric membranes. Journal of Membrane Science 2007;306(1–2):16–28.
[70] Visser T, Koops G, Wessling M. On the subtle balance between competitive sorption and plasticization effects in asymmetric hollow fiber gas separation membranes. Journal of Membrane Science 2005;252(1–2):265–77.
[71] Visser T, Wessling M. Auto and mutual plasticization in single and mixed gas C_3 transport through matrimid-based hollow fiber membranes. Journal of Membrane Science 2008;312(1):84–96.
[72] Kanehashi S, Nakagawa T, Nagai K, Duthie X, Kentish S, Stevens G. Effects of carbon dioxide-induced plasticization on the gas transport properties of glassy polyimide membranes. Journal of Membrane Science 2007;298(1–2): 147–55.
[73] Bos A, Pünt I, Wessling M, Strathmann H. Plasticization-resistant glassy polyimide membranes for CO_2/CO_4 separations. Separation and Purification Technology 1998;14(1–3):27–39.
[74] Merkel T, Lin H, Wei X, Baker R. Power plant post-combustion carbon dioxide capture: an opportunity for membranes, Journal of Membrane Science 2010;359(1–2):126–39.
[75] Coker D, Freeman B, Fleming G. Modeling multicomponent gas separation using hollow-fiber membrane contactors. AIChE Journal 1998;44(6):1289–302.
[76] Biegler LT, Grossmann IE, Westerberg AW. Systematic methods for chemical process design, Prentice Hall, Old Tappan, NJ (United States), 1997, ISBN 0-13-492422-3.
[77] Follmann P. Membrane gas separation processes for post combustion CO_2 capture from coal fired power plants. PhD thesis, RWTH Aachen University; 2010.
[78] Baumgarten G, Boam A, Nasso M, Priske M, Balster J. Membrane based separations in gases and organic liquids. in: Aachener Membran Kolloquium 2010;13.
[79] Makaruk A, Harasek M. Numerical algorithm for modelling multicomponent multipermeator systems. Journal of Membrane Science 2009;344(1–2):258–65.
[80] Makaruk A, Miltner M, Harasek M. Membrane biogas upgrading processes for the production of natural gas substitute. Separation and Purification Technology 2010;74(1):83–92.
[81] Rautenbach R, Welsch K. Treatment of landfill gas by gas permeation—pilot plant results and comparison to alternatives. Journal of Membrane Science 1994;87(1–2):107–18.
[82] Miltner M, Makaruk A, Harasek M. Investigation of the long-term performance of an industrial-scale biogas upgrading plant with grid supply applying gas permeation membranes. Chemical Engineering 2010 21. Klemeš, J.J., Lam, H.L., Varbanov P.S., Copyright © 2010, AIDIC Servizi S.r.l., ISBN 978-88-95608-05-1 ISSN 1974-9791, 〈http://dx.doi.org/10.3303/CET1021203〉.
[83] Favre E, Bounaceur R, Roizard D, Biogas. membranes and carbon dioxide capture. Journal of Membrane Science 2009;328(1–2):11–4.
[84] Kapdi S, Vijay V, Rajesh S, Prasad R. Biogas scrubbing, compression and storage: perspective and prospectus in Indian contextRenewable Energy 2005;30(8):1195–202.
[85] Iniyan S, Sumathy K. An optimal renewable energy model for various end-uses. Energy 2000;25(6):563–75.
[86] Iniyan S, Suganthi L, Jagadeesan T. Renewable energy planning for India in 21st century. Renewable Energy 1998;14(1–4):453–7.
[87] Bond T, Templeton M. History and future of domestic biogas plants in the developing world. Energy for Sustainable Development 2011;15(4):347–354, http://dx.doi.org/10.1016/j.esd.2011.09.003.
[88] Martins das Neves L, Converti A, Vessoni Penna T. Biogas production: new trends for alternative energy sources in rural and urban zonesChemical Engineering & Technology 2009;32(8):1147–53.
[89] Kuwahara N, Berni M, Bajay S. Energy supply from municipal wastes: the potential of biogas-fuelled buses in BrazilRenewable Energy 1999;16(1): 1000–3.
[90] Salomon K, Silva Lora E. Estimate of the electric energy generating potential for different sources of biogas in Brazil. Biomass and Bioenergy 2009;33(9): 1101–7.